OUTLINE OF THE RESEARCH PROPOSAL FOR THE Ph.D. DEGREE IN CHEMISTRY

Title of the topic	:	"Synthesis, Characterization and Catalytic Applications of Mixed Metal Oxides"
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1. Title:

SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATIONS OF MIXED METAL OXIDES

2. Aims of the study

To synthesize metal oxides/ferrites-based composites with g-C_3N_4/MWCNT/Carbon Nanotubes. The resultant composite material will be used in energy applications (supercapacitors) as well as in environmental remediation using model dyes and industrial wastewater from industries as well as ETPs. These applications in environmental remediation and energy are the need of the hour.

3. Objectives:

1. To prepare low-cost and environmentally friendly energy storage systems in response to the needs of modern society and emerging ecological concerns.
2. Synthesized catalyst can be used as a supercapacitor in energy storage.
3. The synthesized doped ferrites (functionalized materials) will be studied for their Gas Sensing properties.
4. New, environment-friendly and low-cost catalyst is to be found, in response to the needs of emerging ecological concerns.
5. Use of Metal oxides and mixed metal oxides (Ferrites) composites in the photodegradation of dyes.
6. Catalyst will be used in various organic transformations or in Organic Conversions like condensation reactions, oxidation, and reductions.

4. Study Background (Literature Review) and significance of the study

During the past decades due to rapid industrialization, there is an increase in pollution at all three levels (air, water, and soil). Due to the increase in the population, there is an increase in the demand for food grain to feed the entire globe. Tremendous use of insecticides, pesticides, and fertilizers to increase the food grains had resulted not only in the pollution of soil but also in polluted water bodies as well as groundwater. Environmental pollution is a burning issue of this century. The disposal of a large amount of wastewater from textile, dyeing, printing, cosmetic, food, photography, and pharmaceutical industries had resulted in environmental pollution. [2-6]. Therefore, it is important that new, environment-friendly, and low-cost catalysts be found, in response to the needs of emerging ecological concerns. The entire world contains only 3% portable water and it is polluted to a great extent by the dye industries, fertilizer industries, pharmaceutical industries, and many more. Hence the issue of water pollution should be addressed immediately.

The demand for energy around the globe is increasing day by day due to the global increase in the human population. It has resulted in a major strain on the existing power of infrastructure and there is a need to find out answers to solve the energy issue. Until now, fossil fuels have been largely used for the power need of the globe. However, with the limited fossil fuel resources, there is a need for alternate energy sources to replace fossil fuels. In recent decades there has been a significant amount of interest in developing new technologies to address energy challenges. In this context, considerable efforts have been put forth to develop more efficient energy storage devices and the systems such as batteries and supercapacitors. Supercapacitors are considered promising candidates for power devices for future generations. These devices are expected to find applications in hybrid electric vehicles and other power devices and systems. For supercapacitor to realize their promise it is important that their energy and power densities should be maximized. It can be addressed by developing advanced and functionalized materials for electrode preparation and developing novel methods to fabricate these materials.

To address the above water pollution, energy storage, and supercapacitor application we need functionalized material. These functionalized materials can be synthesized or achieved with the help of a composite of metal ferrites/ metal oxides with g-C_3N_4/MWCN/Carbon Nanotube, synthesized using the hydrothermal method.

Literature reviews suggest that Graphitic carbon nitride is an intriguing carbon nanomaterial that is widely utilized to design electrode material for supercapacitors because of its ultrathin nanostructure, excellent electric conductivity, and mechanical stability [1]. Recently, researchers have reported a lot of applications of g-C3N4-based transition metal oxide composites as electrochemical materials [1]. The hybrid material can improve electrochemical performance with the synergistic effect between g-C_3N_4 and transition metal oxides. In these systems, g-C_3N_4 works not only as a conductive backbone to facilitate electron transport but also as a mechanical structure that maintains the integrity of the electrode during the electrochemical process [1]. In addition, g-C_3N_4 with metal oxide can be obtained in an economic and promising way to achieve high supercapacitor performance [1].

Thus g-C_3N_4 has become a major research topic in material science due to its versatile applications and as a support material in catalysis [8]. However so far, very less attention has been paid to g-C_3N_4, g-C_3N_4 -oxide-based UV-Visible light driven photocatalyst [9] as well as energy storage devices [10-11].

It is observed that there are many catalysts that are photo inactive under visible light irradiation. However, these photo inactive material when combined with g-C_3N_4 material leads to high photodegradation of methylene blue dye under visible light irradiation [2-7].

In recent years many nanomaterials like graphene, phosphorene, and metal oxide nanosheets have been investigated for gas sensing applications due to their excellent properties. Amongst these graphitic carbon nitrides (g-C_3N_4) have attracted significant attention owing to their simple synthesis process and tunable electronic properties. Such remarkable properties assert g-C_3N_4 as a potential candidate for the next-generation high-performance gas sensors employed in the detection of toxic and flammable gases [31]. Gas Sensors are important for environmental monitoring, home safety, and chemical control. There is an increasing interest in the development of new materials in order to develop high-performance solid-state gas sensors.

Many different semiconducting oxides in bulk ceramic, thick film, and thin film forms have been studied as sensor elements for gas sensing [28-29]. Now a day's ferrites materials are being increasingly studied as gas sensors as their selectivity and sensitivity for some gases are comparatively better than n-type semiconducting oxides.

Spinel-type oxide semiconductors with the formula MFe_2O_4 have been reported to be sensitive materials to both oxidizing and reducing gases. Conduction in spinel ferrites occurs

via transfer of charge carrier (electron or hole) between equal captions located in octahedral sites [30]. Flammable, explosive, and toxic gases, such as hydrogen, hydrogen sulfide, and volatile organic compounds vapor are major threats to ecological environmental safety and human health. Among the available technologies, gas sensing is a vital component and has been widely studied in the literature for early detection and warning. As a metal oxide semiconductor, zinc ferrite ($ZnFe_2O_4$) represents a kind of promising gas sensing material with a spinel structure, which also shows a fine gas sensing performance in reducing gases.

Spinel ferrite $ZnFe_2O_4$ is a semiconductor with a narrow band gap (1.9eV), which possesses various excellent properties. It has attracted much attention in the applications of gas sensors, catalysts, magnetic materials, and lithium battery materials [31].

5. National Status

Development of the country depends largely upon the Industries; Catalyst can be directly link to the health products, medicines, water filters, cosmetics, textiles, bulk chemicals, paints pigments, petroleum and oil industries as well as energy storage materials. Researchers in India are working very hard on the water splitting to produce H2 gas as the renewable source of energy. Researchers in India are also working very hard on the photodegradation of dyes using ferrites as the magnetically separable catalyst over methylene blue as a model dye. However, the composite material of metal oxides/ferrites with graphitic Carbon Nitride/MWCNT/Carbon Nanotubes and its application in energy storage as well as in photodegradation is quite unexplored area of research. Hence there is lot of scope to work on ferrite composite and to study its various applications for the betterment of mankind.

6. International Status

The global energy demands and environmental crisis have stimulated tremendous research on the exploration of green and renewable energy due to awareness of energy conservation and environmental protection. Ferrite and its composites were used in environmental remediation as well as in the water splitting to generate hydrogen, a very clean source of energy [32].

The development and application of magnetic ferrite-based titanium oxide and zinc oxide nanocomposite as catalysts are extremely promising for the removal of organic pollutants from water and wastewater [32].

In the view of above studies at the international level we have planned to work on mixed metal oxides/ferrites doped with graphitic Carbon Nitride/MWCNT/Carbon Nanotubes composites and to study its various applications.

7. Study Hypothesis:

New renewable energy sources and energy storage materials are the two major challenges in electrochemical technology. In this context, the potential application of supercapacitors from simple consumer electronics to Air bus 380S planes has been methodically explored due to their functional ability to link the performance gap between batteries and dielectric capacitors with significantly better power and energy density [12-14]. Among the array of electrode materials for supercapacitor applications, transition metal oxides are widely studied due to variable oxidation states of metal ions which facilitate redox transitions and higher charge storage within the potential range of water decomposition [15].

A supercapacitor is a new kind of energy storage device that receives much attention in recent years due to its long-life cycle, low sensitivity to temperature, high power density, and high efficiency of charging and discharging [16-17]. Ferrite a very important class of metal oxide in combination with g-C_3N_4 and g-C_3N_4 oxide is used in the synthesis of supercapacitors. The capacitance and the charge storage of the electrochemical supercapacitor (ES) depend on the electrode material used. The electrode material of ES can be categorized into three types [18-20].

1. Carbon material with a high specific surface area. [21].
2. Conducting polymers [22].
3. Metal oxides [23].

In general metal oxide can provide higher energy density for ES than carbon material and polymer materials. They not only store energy like electrostatic carbon materials but also exhibit electrochemical Faradic reactions between electrode material and ions within appropriate potential windows [24].

In view of such an important commercial application, the synthesis of metal oxide substituted composite g-C_3N_4/MWCNT/Carbon Nanotubes material is planned. The synthesized composite materials will be characterized and checked for their applications in the field of catalysis.

8. Rationale / Research Hypothesis:

There is an urgent need to develop the green and renewable energy resources to overcome the pollution problems and alsó to meet the energy demand of human being. Hydrogen is the best candidate to replace fossil fuel as it has no impact on the environment. Supercapacitor is a new kind of energy storage devices that receives much attention in recent years. The most important issue the world is facing is clean and pure portable water. The most common industrial effluent is due to dyes and textile industries. They are the most common environmental pollutants at the time of their synthesis and further during dyeing of fibres. Hence pollution issue should be addressed immediately and very efficiently. The research will be carried out to study applications in the field of energy production, environmental remediation for sustainable development.

In view of such an important commercial application, the synthesis of metal oxide substituted composite g-C_3N_4/MWCNT/Carbon Nanotubes material is planned.

9. Research Methodology

The following systems will be synthesized:

1. **Zn_{1-x} $Co_{0.5x}$ $Mg_{0.5x}$ $FeCrO_4$** modified graphitic Carbon Nitride/MWCNT/Carbon Nanotubes (Composites).

2. **Zn_{1-x} $Cu_{0.5x}$ $Mg_{0.5x}$ $FeCrO_4$** modified graphitic Carbon Nitride/MWCNT/Carbon Nanotubes (Composites).

The following methods will be employed for the synthesis of mixed metal oxides/ferrites and composite nanomaterials. The starting materials are nitrates of corresponding metals.

A. Sol-Gel auto combustion method- Aqueous solutions of all the nitrates of metals and citric acid will be taken in the ratio of 1:3 in the minimum amount of distilled water followed by NH_3 solution in order to adjust the pH of the solution at 7. The mixed solution will be kept on the hot plate at 90°C to get a viscous gel. Eventually, the gel gets ignited and the reaction stops when all the citrate in the reaction is consumed. Auto combustion gets completed within a minute, yielding brown-colored ash termed as the precursor. The prepared powder will be fired in a furnace at 900°C for 5 hours, cooled to room temperature, and crushed in the mortar and pestle. The crushed powder will be characterized using various spectroscopic

techniques. The obtained ferrite will be doped with g-C_3N_4/MWCNT/Carbon Nanotube to get the required composite [25].

A. Hydrothermal Method

Synthesis of modified ferrite:

Modified ferrite is synthesized either by In-situ or Ex-situ method.

In-situ: - Nanocomposites of metal salts and graphitic carbon nitride were synthesized by a one-step hydrothermal method via the following process. Different metal nitrites will be dissolved in distilled water by ultrasonic treatment for 30 minutes and to this solution, an appropriate quantity of g-C_3N_4/MWCN/Carbon Nanotube will be added. The resulting mixture will be transferred to an autoclave for the hydrothermal route at 180°C for 6 hours. The product will be collected and rinsed twice with distilled water followed by absolute ethanol and then dried in the oven at 80°C for 24 hours. Finally, a fine white to gray powder will be obtained. Samples will be prepared with the different g-C_3N_4 content as 1, 3, 5, and 7 wt. % [26].

Ex-situ: - Nanocomposite of mixed metal ferrites/ g-C_3N_4/MWCN/Carbon Nanotube will be synthesized by hydrothermal combined calcination method. At first certain amount of metal salts were dissolved in the distilled water. The appropriate pH will be adjusted and then stirred for 15 min to ensure complete precipitation. The obtained product was subjected to hydrothermal treatment at 180°C for 8 hrs. After centrifugation, washing, and drying mixed metal ferrite will be obtained. As synthesized ferrites were doped by varying concentrations of g-C_3N_4/MWCN/Carbon Nanotube followed by sonication [27].

Synthesis of Graphitic Carbon Nitride – Melamine (5 gm) in Silica crucible with lid was heated in the Furnace at 550°C for 4 hours to obtain a light-yellow bulk g-C_3N_4 product. After cooling to room temperature, the light-yellow product will be thoroughly ground with mortar and pestle to obtain a very fine powder of bulk g-C_3N_4. The obtained product was again heated to 550°C for 2 hours to obtain the light-yellow powder of g-C_3N_4 nanosheets [1].

The physical and chemical properties of nanocomposites depend upon chemical composition, method of preparation, and annealing temperatures. Method of preparation plays a very vital role in the properties of composites. Material synthesized by the above methods will be characterized by XRD, FTIR, FESEM, BET, VSM, SQUID (Superconducting quantum interference device magnetometer), GCMS, and Cyclic Voltammetry.

10. Statistical Plan:

0-6 Months Synthesis of Metal Oxides	**6-12 Months** Synthesis of Composites	**12-18 Months** Optimization of the Composites
18-24 Months Applications of Composites	**24-30 Months** Publications & Presentations in Conferences	**30-36 Months** Writing of Synopsis and thesis

11. Limitations of the study:

Timely availability of characterization.

12. Expected Results/Outcomes:

Ferrites synthesized will be confirmed by various techniques such as XRD, FTIR, SEM, BET Surface area, and VSM magnetometer. Cation distribution will be carried out by using the Bertaut method. Rietveld Analysis will be carried out to match the data and the structure will be refined. XRD patterns help to understand ferrite's structure, further, it will be used to find out crystallite size by using Scherrer's equation. Oxygen positional parameters, and ionic radii, will be evaluated by using the Bertaut method or by using Rietveld Analysis.

With FTIR, absorption bands, the bond between Cation and oxygen as well as tetrahedral and octahedral sites will be evaluated. With SEM analysis particle size will be evaluated. Surface area determines the efficiency of the catalyst hence BET as well as Langmuir surface area will be evaluated by the nitrogen adsorption method. With a VSM magnetometer, we will find magnetization in the material. Bertaut method or Rietveld Analysis helps to know cation distribution at the A Site and B site as well as various other parameters. Thus, by using the above technique ferrites will be characterized.

Graphitic carbon nitride will be doped into as synthesized ferrites. The doped material synthesized will be further characterized by the same technique with which ferrites were characterized, such as XRD, FESEM, VSM, BET, etc.

The synthesized doped ferrites (functionalized materials) will be applied to study photocatalysis, Gas Sensing. Further catalysts will be used in various organic transformations or in Organic Conversions like condensation reactions, oxidation, and reductions [4-5]. The catalyst can also be used as a supercapacitor in energy storage. The need of the hour is a supercapacitor an energy storage device. An electrode will be synthesized from g-C_3N_4/MWCN/Nanotube doped ferries material and capacitance will be evaluated using cyclic voltammetry. A graph of current against voltage will be drawn to study the capacitance of the material synthesized.

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